



**WESTERN REGION
HAZARDOUS SUBSTANCE RESEARCH CENTER**

1991 ANNUAL REPORT

Stanford University
Oregon State University

December 1991

Sponsored by the U.S. Environmental Protection Agency

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TABLE OF CONTENTS

ADMINISTRATION 1
THE CENTER AT A GLANCE 1
CENTER DIRECTOR'S REPORT 4

HIGHLIGHTS FOR 1991

RESEARCH ACTIVITIES 6
 Groundwater Management 6
 Chlorinated Solvents 6
 Aromatic Compounds 9
TRAINING AND TECHNOLOGY TRANSFER 11
 Training 11
 Technology Transfer 11
RESEARCH AND TRAINING AND TECHNOLOGY TRANSFER PROGRAM
SUMMARY.14
 Research Program Summary 14
 Training and Technology Transfer Program Summary 16

RESEARCH PROJECT DESCRIPTIONS

CHEMICAL MOVEMENT, FATE, AND TREATMENT 17
CHLORINATED SOLVENTS 20
AROMATICS 26
HEAVY METALS 31
TRAINING AND TECHNOLOGY TRANSFER 33
WRHSRC PUBLICATIONS 35

WESTERN REGION HAZARDOUS SUBSTANCE RESEARCH CENTER

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THE CENTER AT A GLANCE

The Western Region Hazardous Substance Research Center (WRHSRC) is a cooperative activity between Stanford University and Oregon State University that was established in February 1989 to address critical hazardous substance problems in EPA Regions 9 and 10. The Regions include the states of Alaska, Arizona, California, Hawaii, Idaho, Nevada, Oregon, and Washington, and Guam. The Center receives its base financial support from the U.S. Environmental Protection Agency, but also is supported through grants, contracts, and gifts from other federal agencies, states, municipalities, consultants, and industry.

The objectives of the Center are:

1. To promote through fundamental and applied research the development of alternative and advanced physical, chemical, and biological processes for treatment of hazardous substances in the surface and subsurface environments.
2. To disseminate the results of research to the industrial and regulatory communities, to foster exchange of information with these communities, and to promote a better understanding of the scientific capability to detect, assess, and mitigate risks associated with hazardous substance usage and disposal.

Groundwater cleanup and site remediation, with a strong emphasis on biological approaches, represent the major focus of Center activities. The research and training functions of the Center address the major hazardous substance problems in EPA Regions 9 and 10, including chlorinated and nonchlorinated solvents, petroleum products, pesticides, and toxic inorganic compounds including heavy metals. Environmental problems from these substances, which often occur in mixtures, result largely from the production of electronic equipment, chemicals, forestry products, and food, as well as mining and military activities, all of which are important in the region pair. Currently, the Center is overseeing 23 research projects, eight of which are concerned with chlorinated solvents, four involve halogenated aromatic compounds such as pentachlorophenol and PCBs, three address problems with nonhalogenated aromatics, including petroleum derivatives such as gasoline and ordnance wastes such as TNT, two are directed toward solution of heavy metal problems, and six evaluate factors affecting movement and fate of the above chemicals in the environment or address design and management issues for site

cleanup in general. Technology transfer and training activities are broad and include sponsorship of sessions at several major conferences, technical workshops directed toward technology transfer, development of a major training program in Oregon, and numerous presentations of research information and technology transfer at conferences, workshops, and seminars for regulators, industry, consulting firms, and university faculty and students.

The faculty and staff who are directing the Center's research, training, and technology transfer activities are listed in Table 1. They collectively represent an integrated research team representing four different schools (engineering, earth sciences, medicine, and veterinary medicine), and many different disciplines (microbiology, chemistry, hydrogeology, hydrology, chemical engineering, civil engineering, and medicine). Perry L. McCarty is Director of the overall Center and of the research program. Kenneth J. Williamson serves as Associate Director in charge of training and technology transfer and coordinates the Center's overall activities in Oregon. Lewis Semprini is an Assistant Director who coordinates technology transfer and research activities in California. Martin Reinhard is Assistant Director in charge of the Center's analytical program. Marilyn C. King is the Center's Administrative Assistant.

The Center's Science Advisory Committee and Training and Technology Transfer Advisory Committee members are listed in Tables 2A and 2B, respectively, and represent federal and state governments, industry, consulting firms, and universities. The budgets for the past year and the total since the Center's inception are summarized in Table 3. The education of students interested in careers directed toward finding solutions to environmental problems is another important goal. The number of students supported through WRHSRC funds is also listed in Table 3.

Table 1. KEY PERSONNEL AT THE CENTER

<u>Stanford University</u>	<u>Oregon State University</u>
Prof. David L. Freyberg	Prof. Daniel J. Arp
Prof. Steven M. Gorelick	Prof. A. Morrie Craig
Prof. Dunja Grbić -Galić	Dr. Michael R. Hyman
Prof. Lynn M. Hildemann	Prof. James D. Ingle
Mr. Gary D. Hopkins	Prof. Jonathan D. Istok
Mrs. Marilyn C. King	Prof. Peter O. Nelson
Prof. Peter K. Kitanidis	Prof. John C. Westall
Prof. James O. Leckie	Prof. Kenneth J. Williamson
Prof. Abdul Matin	Prof. Sandra L. Woods
Prof. Perry L. McCarty	
Prof. Martin Reinhard	
Prof. Paul V. Roberts	
Dr. Lewis Semprini	

Table 2A. SCIENCE ADVISORY COMMITTEE

<u>Member</u>	<u>Affiliation</u>	<u>Expertise</u>
John J. Barich	Govt/EPA	Regulations
John Conomos	Govt/USGS	Hydrology
Frank Deaver	Industry	Electronics
John F. Ferguson	University	Biological Processes
John Glaser	Govt/EPA	Physical/Chemical Processes
Ronald Hoeppel	Govt/DOD	Microbiology
Michael C. Kavanaugh*	Consulting Engineer	Physical/Chemical Processes
Garrison Sposito	University	Soil Science
James M. Tiedje	University	Microbiology
William A. Wallace	Consulting Engineer	Design
John L. Wilson†	University	Hydrology
John T. Wilson	Govt/EPA	Microbiology
John Wise	Govt/EPA	Planning

*Chairman

†Vice Chairman

Table 2B. TRAINING AND TECHNOLOGY TRANSFER ADVISOR COMMITTEE

<u>Member</u>	<u>Affiliation</u>	<u>Expertise</u>
James T. Allen	Govt/ California	Treatment Technology
Kenneth Bigos	Govt/EPA	Air Pollution
Roy W. Brower	Govt/Oregon	Environmental Quality
Robert Courson	Govt/EPA	Planning
Ethelwyn Hoffman	Govt/Washington	Training
David Kennedy†	Consulting Engineer	Treatment Technology
Jon Kindschy	University	Hazardous Substances Training
Gregory Peterson	Consulting Engineer	Treatment Technology
M. R. Scalf	Govt/EPA	Groundwater Remediation
Kenneth Sutherland*	Industry	Treatment Technology
Winona Victory	Govt/EPA	Training/Tech Transfer

*Chairman

†Vice Chairman

Table 3. CENTER FUNDING

<u>Funding Sources</u>	<u>FY 1991*</u>	<u>Funds to Date</u>
EPA: Centers Program	\$948,568	\$3,874,648
EPA: Other	\$277,816	\$477,816
Other Govt: Federal†	\$390,000	\$970,000
Other Govt: State	0	0
Consortium	\$137,555	\$563,268
Private Sector#	\$660,545	\$1,384,741
TOTAL	\$2,414,484	\$7,270,473

*Oct. 1, 1990 - Sept. 30, 1991

†Department of Energy; Department of Defense

#Allied Signal Corporation; Brown and Caldwell; CH2M HILL; DuPont Corporation; Electric Power Research Institute; Gas Research Institute; Hewlett-Packard Company; Kennedy/Jenks/Chilton; Kleinfelder, Inc.; James M. Montgomery Consulting Engineers Inc.; MBT Environmental Engineering, Ltd.; McLaren/Hart; Orange County Water District; Schlumberger Technologies; Shell Development Corporation

<u>Student Support</u>	<u>Number*</u>	<u>Funds to Date†</u>
Undergraduates	0	0
M.S.	19	\$ 367,000
Ph.D.	45	\$1,547,000
Post Doctoral	7	\$ 401,000
TOTAL	71	\$2,315,000

*Full-Time-Year Equivalent

†Includes tuition, travel, supplies, etc.

CENTER DIRECTOR'S REPORT

With the close of the WRHSRC first project period of three years, it is well to address both its accomplishments and future directions. The WRHSRC now has 18 faculty members representing two universities, seven schools, and five disciplines (engineering, chemistry, microbiology, hydrogeology, and medicine). Twenty-seven research projects have been initiated, and by the end of the third year, all but five will have been completed. Eight new projects have been approved for funding beginning with the fourth year.

The results of the Center's research have been disseminated broadly. To date there have been 75 publications from work supported by the WRHSRC. These include 14 journal publications, with 19 more submitted and under review; one bound proceedings; 15 chapters in books or articles in bound conference proceedings, three project reports, four Ph.D. dissertations, and 19 M.S. theses. There have been over 100 oral or poster presentations on research findings at international, national, and regional conferences, and over 65 oral or poster presentations that represent broad summaries of research for technology transfer. The WRHSRC has sponsored or cosponsored 13 conferences, seminars, or workshops on subjects as diverse as research findings, environmental engineering education, hazardous substance chemistry and management, and the training and technology transfer process. Technology transfer is an important part of the Center's mission, and the above represent our attempt to achieve this. However, in order to learn how to do this better, the WRHSRC hosted in August the Sixth Conference on Environmental Engineering Education and in November a Five Centers' Conference on Technology Transfer.

Most of the WRHSRC's budget is represented by core funding from EPA. However, other federal funds have come to the Center from other branches within EPA, and from the Department of Defense and the Department of Energy, because of the interest these agencies have in the Center's research. In addition, several industrial organizations and consulting engineering firms have contributed support as well in research contracts and gifts. The latter are important to the Center, not only because they represent financial support and cooperative activity with the users of the Center's research, but they also help achieve the minimum of 20 percent non-federal support that is required for the EPA-sponsored HSRCs.

The WRHSRC is now in the planning and proposal-writing stages for the second project period of five years. The core EPA funds will be somewhat reduced from what they were in the past, which means that the number of projects that can be funded by core support will be reduced. This is causing us to focus considerably. The major research theme for the Center has become the remediation of groundwater contamination. This focus is expected to remain. The contaminants that we have been addressing are the chemical groundwater contaminants that are found with greatest frequency at contaminated sites; these are chlorinated solvents and their degradation products, aromatic hydrocarbons associated with petroleum contamination, halogenated aromatics, and heavy metals.

One of the major findings of recent years is that chlorinated solvents are transformed in groundwater by both chemical and biological processes. The thrust group associated with this problem is directing its efforts toward finding engineering methods for enhancing these natural processes to produce harmless end products. This is closely associated with the related effort to determine

how best to remove polluted groundwater and contaminants from the subsurface environment. The major efforts underway here will continue.

The thrust group studying aromatic compounds are focusing on anaerobic processes. A great deal of evidence has been obtained that aromatic compounds are often transformed in groundwater naturally by microorganisms living under anaerobic conditions. The anaerobic conditions result when the quantity of contaminants present exceed the available oxygen supply, which is often the case. The basic research ongoing here is directed toward predictions of transformation rates, transformation products, and engineering methods that might enhance the rates of desired anaerobic transformations. It may be that in many cases, the most environmentally sound and least expensive alternative is the no-treatment alternative. However, in order to justify this, we must first learn how to make sound judgements about transformation potential at any given location. Research on these major issues will continue.

A third associated thrust area is the modeling of transport and fate processes and groundwater-management strategies. In order to remove polluted groundwater and associated contaminants, improved mathematical models are desirable that consider the great uncertainties in the hydrogeological structure of a contaminated site, and the relative chemical and physical properties of both the contaminant and the aquifer materials that impact on contaminant distribution and movement. An additional highly complex need is for methods to introduce nutrients or other chemicals required to enhance biological or chemical transformation, and to mix these chemicals with groundwater contaminants. The absence of good methods for this is one of the major barriers to in-situ treatment. The models and engineering methods being developed here have direct impact on the activities of the other two thrust groups described above so that good interactions between the three thrust groups is necessary.

A fourth thrust area of the WRHSRC is concerned with heavy metals. Chromium and lead are among the most frequently found hazardous substances found at contaminated sites. The WRHSRC has been conducting research both on improved procedures for removing heavy metals from groundwater, and also on surface treatment of heavy-metal-contaminated groundwater. While we believe it is important to expand these efforts, the current funding situation makes it difficult to do this and to keep strong programs in the other three thrust areas as well. Thus, unless additional support can be found, efforts here may be further reduced or discontinued.

We anticipate somewhat of a change in the training and technology transfer program in coming years. During the first three years, the focus developed by Dr. Kenneth J. Williamson, Director of this Center activity, was in developing in Oregon an extension program of courses dealing with hazardous chemicals, patterned after the highly successful California Extension Program carried out by the University of California system. This is now in place. In addition, with three years of research nearly completed, the WRHSRC believes it is time to place a major emphasis on putting into practice the results of our research investigations. We hope to accomplish this by moving from the first phase of technology transfer, which is research and discovery, further into the second phase of user awareness and information exchange, into the third phase of field pilot-scale demonstration, and to the extent possible, into the fourth phase of full-scale application. We are presently conducting third-phase activities with our Moffett Field and Seal Beach pilot investigations, and are working toward the fourth phase at the St. Joseph Superfund site, where we have proposed and are in the design stage for in-situ bioremediation. We also hope to

continue these and other technology transfer activities in a more formalized and evaluative way during the coming year in order to develop a better understanding of the technology transfer process.

We have an ambitious agenda for the coming years. The accomplishments of the past three years suggest that we should be able to achieve our goals. However, in order to do this we will need financial and moral support from the many interested parties, including the various branches of the federal and state governments, industry, and the consulting community. Highlights of accomplishments this past year in our research thrust groups and our training and technology transfer program are described below.

HIGHLIGHTS FOR 1991

During this past third year of WRHSRC activity, many research tasks have been completed, resulting in numerous publications and presentations on research findings. Some of the most significant activities in the three major thrust areas, that address groundwater management and groundwater contamination with chlorinated solvents and aromatic compounds, are singled out for highlighting this year. Unless otherwise indicated references in the text refer to reports listed under Center Publications.

RESEARCH ACTIVITIES

Groundwater Management

The Pump and Treat strategy is often used for removing contaminants from aquifers. The statistical and simulation foundations of the simulation-optimization approach being studied by the WRHSRC enable one to evaluate the reliability of model predictions and to determine appropriate levels of overdesign for achieving reliable remediation. Analysis of the contamination problem at the Gloucester landfill Special Waste Compound in Canada was conducted using a new modeling approach which determines aquifer properties from the simultaneous analysis of both hydraulic head and concentration data (Gailey and Gorelick, 1991; Gailey et al., 1991). This "coupled-process modeling approach" takes advantage of the fact that head and concentration data provide valuable independent information about the aquifer properties that control subsurface fluid flow.

When the coupled-process modeling approach was applied to the Gloucester contaminant problem, predictions of peak concentrations had 95% confidence limits which were within 12% of the peak values. If aquifer properties had been estimated using head data alone, the width of the confidence bounds on peak concentrations would have exceeded the peak values themselves, indicating almost no predictive reliability. Uncertainty in prediction implies that remedial systems must be over-designed to assure contaminant capture, yet over pumping is a waste of resources that tends to mix uncontaminated and contaminated groundwater. For the Gloucester site, to assure the success of a remedial scheme for contaminant capture, the optimal (minimal) pumping rates required an overdesign safety factor of 1.3, or 30% extra pumping.

Chlorinated Solvents

Eight of the Center's projects are concerned with chlorinated solvents, the most common chemicals at contaminated sites. Three represent basic research studies on biotransformation of chlorinated aliphatic compounds. These range from studies on the kinetics of transformations by methane oxidizing (methanotrophic) bacteria to the development of recombinant strains of bacteria to maintain high biodegradation activity under environmental stress conditions. A related project addresses abiotic transformations. A fifth project is directed toward determining factors affecting the rates of sorption and desorption in heterogeneous soils because of its general importance to any form of remediation. With the success at the WRHSRC's Moffett Field demonstration of in-situ biodegradation of chlorinated aliphatic compounds by methanotrophic bacteria, activities leading toward the design of a full-scale pilot test of this process at the St. Joseph, Michigan, Superfund site took place this past year. This represents our first major

attempt to carry through the complete process of technology transfer from initial laboratory development to full-scale application. This past year's efforts include the development of a process for subsurface mixing of methane and oxygen with contaminated groundwater, modeling of the subsurface mixing and biotransformation processes, laboratory evaluation of kinetics of transformation by indigenous methanotrophic bacteria, and design of the pilot plant facilities. Finally, the first phase of a comparative field and laboratory evaluation and demonstration of the toluene oxygenase (TO) system for in-situ biotransformation was completed this year. Some of the findings from these studies are briefly described in the following.

Chlorinated Aliphatic Transformation Rates

Methanotrophic bacteria produce methane monooxygenase (MMO) to initiate the oxidation of methane, which they use as a carbon and energy source. This nonspecific enzyme fortuitously initiates oxidation of many chlorinated aliphatic compounds as well, including trichloroethylene (TCE), cis- and trans-1,2-dichloroethylene (cis-DCE, trans-DCE), vinyl chloride (VC), and chloroform (CF). This is termed cometabolism. The potential for the MMO system was first reported in 1985 by J. T. Wilson and B. H. Wilson [*Applied and Environmental Microbiology*, 49, 242-243 (1985)]. A most important finding from this past year's studies is that the intermediate compound formed from TCE transformation (TCE epoxide) transforms spontaneously to products, some of which damage or kill the cells (Alvarez-Cohen and McCarty, 1991a,b,d; Henry and Grbić -Galić, 1991a). This transformation product toxicity has several consequences for the methanotrophic process. One is that more methane must be supplied to grow new cells in order to maintain the process. Measures of this effect are represented by the transformation capacity (T_c) and the transformation yield (T_y). The maximum T_c values for a resting mixed culture of methanotrophic bacteria were found to be 0.042 g TCE per g cells and 0.0083 g CF per g cells. With addition of reducing power in the form of formate or methane, T_c increased somewhat, but still is finite. This means, for example, that one milligram of methanotrophic mixed culture would be expended or killed by transformation products by the time it had transformed 0.042 mg of TCE. T_y is a measure of the mass of contaminant transformed per unit mass of methane used to grow the methanotrophs. T_y was found to be 0.026 g TCE transformed per g methane consumed. The effect of T_c on reaction kinetics was evaluated, and a novel two-stage above-ground biological treatment system for chlorinated aliphatic compounds was proposed (Alvarez-Cohen and McCarty, 1991c).

A second consequence of transformation product toxicity is that the growth of methanotrophic bacteria in an aquifer or treatment system is impeded by the presence of TCE. This has been confirmed for a reactor system, and the nature and extent of this potential problem is now under evaluation for in-situ bioremediation. In a comparative evaluation for other halogenated aliphatic compounds, T_c has been found to increase in the order: 1,1-DCE, CF, TCE, 1,2-DCE, VC. In addition, when these compounds are present together, the relative rates of transformation of each compound is affected by competitive inhibition kinetics as well as by the relative product toxicity. These factors all need to be considered for in-situ and above-ground treatment systems.

St. Joseph Superfund Site

In-situ methanotrophic groundwater treatment of chlorinated aliphatic compounds was proposed by the WRHSRC for evaluation at the St. Joseph, Michigan, Superfund site. Here, the original TCE contamination has been transformed naturally by anaerobic (methanogenic) processes to cis- and trans-DCE, and VC, each of which is present in mg/L concentrations. A recent detailed characterization at the location of a proposed full-scale pilot demonstration of in-situ bioremediation was carried out by the industry involved, their consulting engineering firm, and the EPA Robert S. Kerr Environmental Research Laboratory. Further reduction of VC to ethylene was confirmed. These results now suggest that natural anaerobic in-situ bioremediation to harmless end products is being carried out to some extent. The possibility exists that this natural anaerobic process can be further enhanced, and this is proposed for further evaluation. The WRHSRC is also proposing that in-situ aerobic methanotrophic treatment be used as a polishing step to transform remaining VC at this site (McCarty et al., 1991). The site is

relatively simple, hydrogeologically. The groundwater is about 10 m below the surface in a relatively uniform fine-sand aquifer that is between 10 m and 18 m deep.

The St. Joseph study is being carried out cooperatively with Allied-Signal Corporation, Engineering-Science, the Michigan Department of Natural Resources, EPA Region V, the EPA Robert S. Kerr Laboratory, and the WRHSRC. Aseptic core samples obtained by the Kerr Laboratory were examined using protocols developed by the WRHSRC, and found to contain a small population of methanotrophic bacteria that carried out methanotrophic transformations at rates similar to the Moffett Field microorganisms. Sorption of contaminants to the sand was relatively small. The site where in-situ treatment is proposed lies on property owned by others, and for this reason there is a need to employ a nonintrusive treatment system. In addition, VC does not sorb well onto activated carbon and cannot be discharged to the atmosphere. These constraints has led to the design of an underground recirculation system where contaminated groundwater, methane, and oxygen are brought together, mixed, and then recirculated back into the aquifer for biological degradation. Several methods for introduction of methane and oxygen are being evaluated, and laboratory studies on a subsurface system for gas introduction is being developed. Mathematical models of the mixing process and the resulting distribution of biological growth have been developed and are being used to design the pilot-scale facility and monitoring system to evaluate treatment effectiveness.

Previous studies have indicated that high concentrations of chlorinated solvents are not toxic to the methanotrophic bacteria. However, the recent finding of TCE transformation product toxicity suggests that growth of bacteria may be hindered when TCE is present. Additional laboratory studies using core material from the St. Joseph aquifer are now being conducted in order to evaluate the nature of this problem.

The St. Joseph site has presented a challenge to the WRHSRC, and has helped define important research questions for further pursuit. It has also offered the opportunity to bring together individuals from the various disciplines within the Center, and the various interested parties associated with the St. Joseph site. Such cooperative activity is required in order to help solve the new and difficult problems posed. It is expected that the technologies for subsurface mixing will be useful for remediation of other contaminants, where the addition of chemicals for enhancing contaminant mobility as well as transformation may be required.

Field Demonstration with Toluene Oxygenase

The first controlled field demonstration of in-situ cometabolic bioremediation of chlorinated aliphatic compounds by the MMO system was conducted at the Moffett Field Naval Air Station in Mountain View, California by WRHSRC staff [P. V. Roberts et al., *In-Situ Aquifer Restoration of Chlorinated Aliphatics by Methanotrophic Bacteria*, EPA/600/2-89/033, U.S. EPA Center for Environmental Information, Cincinnati, OH (July 1989)]. During this past year, a new demonstration was conducted to obtain a comparative evaluation of the effectiveness of a different enzyme system, the toluene oxygenase (TO) system. The potential for this system was first demonstrated by M. J. K. Nelson et al., *Applied and Environmental Microbiology*, 53, 949-954 (1987). The Moffett Field evaluation was supported through the WRHSRC by a combination of core funds, the EPA Biosystems Technology Initiative, and the Department of Energy. This study is headed by G. H. Hopkins and L. Semprini. Phenol was injected into the Moffett Field aquifer in order to stimulate growth of bacteria containing TO. The thickness of

the confined aquifer used is about 1.5 m, and lies at a depth below ground surface of 4.5 to 6 m. The test site consists of an injection well, where phenol, oxygen, and the halogenated aliphatic compounds (HACs) were introduced, and an extraction well located 7 m away. In line between the injection and extraction wells are three monitoring wells. The time of water travel between the injection and extraction wells is about two days. An automated data acquisition system permitted semi-continuous concentration measurements for bromide tracer, dissolved oxygen, phenol, pH, TCE, cis-DCE, and trans-DCE.

With the MMO system, transformations at the Moffett Field site were approximately: TCE-20%; cis-DCE, 45%; trans-DCE, 90%; and VC, 95%. However, with the TO system, transformations were quite different: TCE-90%; cis-DCE-95%; and trans-DCE, 15%. VC was not evaluated in the latter. The much greater transformation of TCE and cis-DCE by the TO system is most encouraging. TCE and cis-DCE are often the most prevalent compounds found at many contaminated sites. Surprisingly, trans-DCE transformation was much lower than with the MMO system. Thus, depending upon the compounds present, the MMO or the TO system may be the most preferred. This study helps confirm the results of several laboratory and field studies by others that have indicated similar relative rates of transformation of compounds by the MMO and TO systems noted above. Details of this study are being summarized in a paper to be submitted for publication soon.

Phenol was added in the above system both because of its ease in use and its demonstrated effectiveness by others. However, low residual concentrations of phenol has the potential to cause taste and odor problems in drinking water when chlorinated. Toluene is also effective in stimulating the TO system, but its concentration in drinking water is regulated with an MCL of 1 mg/L. Thus, another method for stimulating the TO system is desirable. The above results support the importance of a search for such a method, and the continuation of this path of research for in-situ biodegradation of halogenated aliphatic compounds.

A common method for removing chlorinated solvent contamination from the unsaturated (vadose) zone is vapor stripping. Important questions for remediation are what is the relative fraction of contaminant residing in the sorbed versus the vapor phase in the vadose zone, and what is the rate of desorption from the sorbed phase. A chromatographic technique was developed this past year to help answer both these questions (Farrell and Reinhard, 1991). This method indicated that sorption isotherms of TCE and low-organic aquifer material were nonlinear. The degree of sorption correlated with solid surface area and organic content. Desorption rates were slow in sandy Santa Clara Valley, California, aquifer material, either because of strong sorption at low vapor pressure, or because of slow desorption rates from strongly sorbing micropores. In contrast, desorption was relatively fast from Norwood soil montmorillonite, which is nonporous and of high-organic content, and from a silica gel. A tentative conclusion is that particles containing micropores may cause slow desorption, leaving high residuals in soil gas evacuation schemes, a possibility that deserves attention for design of remediation schemes.

Aromatic Compounds

One of the major interests of the WRHSRC thrust group, who are studying biotransformations of halogenated and nonhalogenated aromatic compounds, is on anaerobic transformations.

Aquifers heavily contaminated with organic materials tend to be anaerobic, and transformations, if they are to occur, must then be through the action of anaerobic consortia of microorganisms. Research in this area has been pioneered by WRHSRC staff. Studies are being conducted on anaerobic transformations of PCBs, pentachlorophenol (PCP), the soluble components of gasoline (benzene, ethylbenzene, toluene, and xylenes, which are collectively termed BTEX), polycyclic aromatic hydrocarbons (PAHs), and heterocyclic compounds containing oxygen, sulfur and nitrogen. In addition, a novel study is underway to evaluate the potential for aerobic cometabolism of PCBs by methanotrophic bacteria.

At the Seal Beach, California, field site, three bioreactors have been placed into the ground and filled with native soil that was contaminated with gasoline. The objective of this study, headed by Prof. M. Reinhard, is to determine the potential of natural transformation processes for BTEX. The reactors have been continually charged with contaminated anaerobic groundwater which contained approximately 5 mg/L nitrate and 70 mg/L sulfate. The behavior of BTEX compounds was monitored over a period of several weeks. Toluene and m,p-xylene removals appeared to occur without adaptation time. The removals of o-xylene and benzene appeared to increase with time, but biotransformation of the latter, which has been found to resist biotransformation, remains to be confirmed. Nitrate was removed nearly quantitatively with BTEX disappearance, while the sulfate concentration remained essentially unchanged. In laboratory microcosm studies with Seal Beach material, anaerobic toluene degradation with sulfate reduction was observed and confirmed with ^{14}C tracers (Haag et al., 1991; Edwards et al., 1991a,b). Confirmation in the field bioreactors is being attempted. There is potential that biotransformation under sulfate-reducing conditions could play a significant role in the clean-up of contaminated aquifers, especially at locations near the ocean and in landfills where the sulfate concentration is high.

During this past year the transformation of acenaphthene (a PAH) and quinoline (a nitrogen heterocycle) under sulfate-reducing conditions has been observed for the first time by the research team headed by Prof. D. Grbić-Galić. The sulfate-reducing microcosms were derived from a largely anoxic, creosote-contaminated groundwater aquifer (Pensacola, Florida). The early intermediates of these anaerobic transformations are 1-acenaphthenol from acenaphthene, and 2-quinolinol from quinoline, respectively. These intermediates are oxidized compounds and probably arise through the addition of a hydroxy-group from water (there is no oxygen present in the microcosms). 1-Acenaphthenol persists in the microcosms, whereas 2-quinolinol is degraded further to unknown products. The initial oxidation reactions correspond to what had been observed with the identical aromatic compounds under methanogenic conditions. However, in these sulfate-reducing microcosms, the oxidations are almost certainly linked to sulfate reduction: the oxidation of the aromatic substrate and sulfate reduction occur concomitantly, and there is a long lag (20 days) before the oxidation of quinoline starts in the absence of sulfate. Subsequent degradation might be the result of methanogenic activity which is gradually enriched in the absence of sulfate. These results suggest that sulfate-reducing communities may also play an important role in degradation of complex aromatic compounds in the anaerobic habitats preexposed to petroleum or creosote contamination.

In another study begun this past year, initiation of the aerobic degradation of PCBs by methanotrophic bacteria through cometabolism is being evaluated. These organisms were found to cometabolically hydroxylate different PCB congeners. Furthermore, the PCBs transformed

included relatively "difficult" ortho-isomers, such as 2-monochlorobiphenyl (2-MCB), 4-MCB, 2,4-dichlorobiphenyl (2,4-DCB), 2,4'-DCB, 2,2'-DCB, and 2,3-DCB. Most of these PCBs were transformed by both pure culture (*Methylomonas* sp. MM2) and mixed culture MM1. These cultures were previously enriched from the Moffett Field groundwater aquifer and shown to transform chlorinated aliphatic solvents. In one case (2-MCB transformation by MM1), the transformation products include a hydroxylated 2-MCB (with the hydroxy-group on the chlorinated ring), a mononuclear aromatic, and a C₂-aliphatic compound. It is of significance that *Methylomonas* sp. MM2 produces only a particulate form of the methane monooxygenase (MMO), which is believed responsible for the PCB and chlorinated solvent transformations. These findings contradict literature which suggests that only the soluble form of MMO can cometabolically oxygenate various organic pollutants. Obviously, methanotrophic bacteria and communities have significant potential which deserves further exploration.

Research on aerobic and anaerobic biotransformation of pentachlorophenol (PCP), sorption effects, and fate and transport modeling has continued within the research group headed by Profs. S. Woods, K. Williamson, and P. Nelson. PCPs are commonly associated with wood-bleaching and preserving operations. Reductive dehalogenation by unadapted anaerobic consortia occurred at the ortho position, leading to the formation of 2,3,4,5-tetrachlorophenol and 3,4,5-trichlorophenol. However, with adapted anaerobic cultures, concurrent dehalogenation at the ortho, meta, and para positions occurred. Rates of anaerobic biotransformation decreased with decreasing degrees of chlorination. For adapted cultures, the fastest removal occurred at the para position. Dichlorophenols, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, and 2,3,5,6-tetrachlorophenol were produced more rapidly than they were removed, and so tended to accumulate in the culture. On the other hand, 2,3,4,5- and 2,3,4,6-tetrachlorophenols were dehalogenated at rates faster than produced so that they did not tend to accumulate. Aerobically, the reverse occurs, the most rapid biotransformation occurs with a lower degree of chlorination of the benzene ring. In studies of PCP adsorption to activated carbon, the process was found to be reversible and competitive, with 93% of maximum sorption occurring within 72 hours.

TRAINING AND TECHNOLOGY TRANSFER

During this year, several training and technology transfer projects were completed. These include the development of a program of hazardous substance training within the State of Oregon through its community college system, the development of a series of continuing education courses for professionals seeking additional education in the hazardous substance area, and the sponsorship of a number of conferences and workshops.

Training

A curriculum in hazardous material management training and education has been sponsored by the WRHSRC and established through a consortium of community colleges in Oregon. A series of four training levels was established and supportive educational curricula were developed to include an 8-hour course for small-quantity generators, a 40-hour course for hazardous material handlers and emergency responders, a one-year curriculum for hazardous material technicians, and a two-year Associate Arts degree in hazardous materials management. The designs of many of the courses are based upon materials provided through the WRHSRC's cooperative venture with the University of California Extension Service Program in Hazardous Material Management.

A six-course sequence for continuing education in hazardous substance management has been developed by the WRHSRC that will be offered through Oregon State University's Department of Continuing Education. The courses are taken by non-degree-seeking professionals presently employed in the hazardous substance field. The WRHSRC is examining ways to expand the distribution of these courses.

In August, the WRHSRC cosponsored at Oregon State University the Sixth Conference on Environmental Engineering Education. Kenneth Williamson, the WRHSRC's Director of Training and Technology Transfer cochaired the event with Dr. H. Gerald Schwartz, Jr., President of the American Academy of Environmental Engineers, one of the cosponsoring organizations. The other cosponsor was the Association of Environmental Engineering Professors. The meeting was financially supported by the National Science Foundation. One of the main topics of this conference, attended by 150 environmental engineering faculty and professionals, was how best to incorporate hazardous substance topics into environmental engineering curricula.

Technology Transfer

One goal of the WRHSRC's training and technology transfer program is to inform potential users of the Center's research activities. This is being accomplished through advanced workshops, sponsorship and participation in conferences, and the presentation of seminars to universities, industry, consulting firms, and regulatory agencies. The WRHSRC was also involved in the planning and implementation of seven conferences related to technology transfer this year.

The WRHSRC cosponsored the International Symposium on "In-Situ and On-Site Bioreclamation," held in San Diego, California, in March 1991, which had over 700 attendees. The Center organized and chaired the sessions on chlorinated solvents, and presented six papers at the

Conference. The Conference Proceedings have been published in two volumes by Butterworth Press.

In November, the WRHSRC sponsored the Five-Centers' Conference on Technology Transfer at Fallen Leaf Lake, California. The purpose was for representatives of the five EPA-sponsored HSRCs and state and federal personnel to learn how to accomplish their technology transfer missions more effectively.

Other WRHSRC cosponsorships included the 1991 Regional Conference on Hazardous Materials and Wastes in Pocatello, Idaho; The National Conference of the National University Continuing Education Association; and the 1991 Responsible Hazardous Materials Management Conference and Trade Show in Portland, Oregon.

The fourth offering of the advanced one-day-course on "Biological Transformation of Chlorinated Solvents in Subsurface Systems" was given in Pasadena in October 1991 through the University of California Extension Program on Environmental Hazard Management. The course will be offered next at the HAZMACON, 92 Conference in Long Beach, CA, in March 1992, as will a WRHSRC-sponsored course on analytical methods.

In addition numerous invited presentations have been given by members of the Center faculty and staff. Included were four seminars in the EPA's Region 9 Superfund Seminar Series. Also, presentations were made at Superfund Research Conferences such as the U.S. EPA, Groundwater Seminar, and the U.S. EPA Biosystems Program. Staff participated in the Bioremediation Workshop on "Translating Laboratory Results into the Field," AgBiotech, Rutgers University, and at the Waste Management Education and Research Consortium Teleconference on "Soil and Groundwater Remediation," which was telecast from Albuquerque. Special seminars were also given to California Regulatory groups such as the Regional Water Quality Control Board and the Department of Health Services. Other seminars were given at the University of California, Berkeley; University of California, Los Angeles; San Jose State University; the University of California System Toxic Substance Program; and Rutgers University. Presentations were also made to members of the WRHSRC Affiliates Program and Industrial Sponsors such as the Electric Power Research Institute.

**RESEARCH AND TRAINING AND TECHNOLOGY TRANSFER
PROGRAM SUMMARY**

RESEARCH PROGRAM SUMMARY

Chemical Movement, Fate, and Treatment

Reinhard, 1992 Grbić -Galić , Leckie, McCarty, Roberts (\$274k total/\$93k current year)	Treatment of Complex Mixtures
Gorelick 1992 (\$174k total/\$58k current year)	Design of Reliable and Cost-Effective Mitigation Schemes
Reinhard, 1992 Roberts (\$191k total/\$63k current year)	Gaseous Stripping of Nonaqueous Liquids from the Vadose Zone
Kitanidis 1991 (\$188k total/\$64k current year)	Detection and Assessment of Subsurface Contamination
Kitanidis, 1991 Freyberg (\$53k total/\$53k current year)	FASTCHEM, Applications and Sensitivity Analysis
Hildemann, 1992 Roberts (\$141k total/\$69k current year)	Dispersion Modeling of Volative Organic Emission from Ground-Level Treatment Systems
Chlorinated Solvents	
McCarty, 1991 Roberts (\$260k total/\$80k current year)	Oxidation of Chlorinated Solvents by Methanotrophs
McCarty, 1992 Roberts (\$230k total/\$84k current year)	Effects of Sorption on Biodegradation of Halogenated Organics
Reinhard, 1991 McCarty (\$80k total/\$25k current year)	Long-Term Chemical Transformation of 1,1,1-Trichloroethane (TCA) and Freon 113 Under Aquifer Conditions
Matin, 1992 Grbić -Galić (\$149k total/\$74k current year)	Use of Starvation and Stress Promoters for Biodegradation of Hazardous Wastes

Chlorinated Solvents (cont.)

McCarty, 1991
Kitanidis,
Roberts,
Semprini
(\$90k total/\$90k current year)

Subsurface Mixing of Nutrients and Groundwater for In-Situ Bioremediation

McCarty, 1992
Roberts,
Semprini
(\$584k total/\$399k current year)

Test-Bed Evaluation of In-Situ Bioremediation of Chlorinated Aliphatic Compounds by Toluene

McCarty, 1991
Roberts,
Gorelick,
Kitanidis,
Semprini
(\$200k total/\$200k current year)

Demonstration of In-Situ Bioremediation of Chlorinated Aliphatics by Methanotrophs at St. Joseph

Roberts 1992
(\$145 k total/\$72k current year)

Determining and Modeling Diffusion-Limited Sorption and Desorption Rates of Organic Contaminants in Heterogeneous Soils

Aromatic Compounds

Woods 1992
(\$139k total/\$49k current year)

Interactions between Electron Acceptors in the Treatment of Wastewaters Containing Sulfate, Chlorophenols and Acetate

Williamson, 1992
Nelson
(\$168k total/\$58k current year)

Enhancing Biodegradation with Sorption with Alternating Aerobic/Anaerobic Environments

Istok, 1992
Woods
(\$166k total/\$62k current year)

Development and Verification of a Numerical Model to Predict the Fate and Transport of Chlorinated Phenols in Groundwater

Grbić -Galić 1992
(183k total/\$62k current year)

Anaerobic Microbial Transformation of Homocyclic and Heterocyclic Polynuclear Aromatic Hydrocarbons

McCarty 1992
Grbić -Galić
(\$102k total/\$102k current year)

PAH Degradation by Methanotrophic Bacteria

Reinhard, 1992
McCarty
(\$410k total/\$150k current year)

In-Situ Biological Treatment of Aromatics in Groundwater

Aromatic Compounds (cont.)

Grbić -Galić 1992 (\$134k total/\$69k current year)	Aerobic Methanotrophic and Anaerobic Transformation of Biphenyl, Monochlorobiphenyls, and Dichlorobiphenyls
Craig Woods 1992 (\$306k total/\$122k current year)	Biotransformation of Ordnance Wastes Using Unique Consortia of Anaerobic Bacteria

Heavy Metals

Leckie 1992 (\$204k total/\$69k current year)	Trace Metal Removal Processes
Nelson, Istok 1992 (\$100k total/\$52k current year)	Hexavalent Chromium Sorption and Desorption in Natural Soils and Subsoils

TRAINING AND TECHNOLOGY TRANSFER PROGRAM SUMMARY

Williamson 1992 (\$45k total/\$15k current year)	Hazardous Waste Training
Semprini 1992 (\$60k total/\$20k current year)	Advanced Topic Workshops
Williamson 1992 (\$45k total/\$15k current year)	Continuing Education Program
Williason, Semprini 1992 (\$30k total/\$10k current year)	Conference Sponsorship

RESEARCH PROJECT DESCRIPTIONS

CHEMICAL MOVEMENT, FATE, AND TREATMENT

Treatment of Complex Mixtures: Martin Reinhard, Dunja Grbić -Galić , J. O. Leckie, P. L. McCarty, and P. V. Roberts, Stanford University.

Goal: The goal of this project is to apply a computer-aided information system to the problems of hazardous waste treatment.

Rationale: When designing treatment processes and assessing the risk of complex hazardous wastes, numerous complex and interrelated factors must be considered, foremost the biodegradability and the physico-chemical characteristics of the contaminants. However, such data are not available except for the most common contaminants. Using computer-based property estimation techniques and process simulation, pilot studies can be designed with considerable cost savings.

Approach: An information system is being used to analyze in detail the performance of single- and multi-step treatment plants for which the removal efficiencies of a broad range of contaminants have been characterized. In these cases, substance properties relevant to treatment of contaminated waters, such as aqueous solubility and n-octanol/water partition coefficients as a function of treatment conditions, are being correlated with observed removal rates during air-stripping, activated-carbon treatment and reverse osmosis. Biological properties will also be considered.

Status: Detailed analysis of air-stripping and activated-carbon treatment has been completed, and analysis of multi-process treatment trains including reverse osmosis and biological processes should be completed by March 1992.

Client/Users: Consultants, educators and regulators interested in treatment plant design for complex mixtures, and researchers studying the relationship between properties and environmental fate of contaminants.

Design of Reliable and Cost-Effective Mitigation Schemes: Steven M. Gorelick, Stanford University

Goal: The aim of this project is to develop and test methods for design of pump-and-treat aquifer remediation systems. These methods can target reliable strategies that identify the best well locations and pumping rates to ensure capture of contaminant plumes. Reliable designs must be based on reliable predictive models. Quantifying both model parameter uncertainty and consequent prediction uncertainty is a major research goal.

Rationale: Simulation models can be powerful tools for designing aquifer remediation schemes. Unfortunately, there is tremendous uncertainty associated with our predictive models of subsurface contaminant transport, even for substances whose chemical behavior is well understood. Given this uncertainty, one must over-design any pump-and-treat system.

Knowledge of the nature of simulation model uncertainty and the development of risk-based design strategies are therefore essential.

Approach: The project is being conducted in cooperation with Environment Canada, and focuses on the Gloucester Special Waste Compound in Ontario, Canada. In 1989 design began for pump-and-treat remediation to remove hazardous organic solvents. The best remediation design requires optimal well selection and the determination of optimal pumping rates. The problem is being approached by developing stochastic simulation models based upon available field data. Then these models are combined with nonlinear optimization methods in order to identify reliable design strategies. Model parameter uncertainty is considered to be a key indicator of design reliability. In this approach, model parameters are first described statistically. This quantification of uncertainty in model input is then translated into confidence bounds on model predictions of contaminant transport. The reliability indicated by the predictive model is then used to over-design the remediation system to the extent necessary to insure success.

Status: An optimization model was constructed and run for remediation of a single plume at the Gloucester site which accounts for parameter uncertainty. Parameter estimates and uncertainties were obtained using the coupled-process approach developed earlier. It was found that achieving 90% reliability of remediation required about 30% over-design of the pumping system. Recently, a model was developed for optimal remediation of three plumes that each travel at different retarded velocities. Pumping from two wells proved to be optimal for the multiple-plume system and required about three times the pumping compared to removal of a single plume. Finally, work was initiated to consider plume migration and potential remediation when transport is mediated by mass-transfer kinetics. Completion is expected by March 1992.

Client/Users: Engineers and hydrogeologists involved in aquifer remediation design; ground-water modelers interested in parameter estimation methods.

Gaseous Stripping of Nonaqueous Liquids from the Vadose Zone: Martin Reinhard and Paul V. Roberts, Stanford University.

Goal: The objective of this study is to gain a better understanding of the factors that control the efficiency of vapor-phase stripping of volatile contaminants from the vadose (unsaturated) zone.

Rationale: Vapor stripping is becoming an increasingly popular method of removing volatile organics from the unsaturated zone. However, there is no basis for assessing when conditions are favorable for this process, nor is there any way of predicting the rate and extent of removals.

Approach: This investigation is divided into three areas. The first is the measurement of organic vapor sorption isotherms for trichloroethylene on a range of different solids. The second involves measuring the rate at which the organic solvents desorb from the soils under vapor-stripping conditions. The third encompasses computer modeling of the stripping process using the isotherm and kinetic data obtained in the other two phases of the project.

Status: A novel methodology has been developed to measure adsorption isotherms under conditions of the unsaturated subsurface environment. Three aquifer materials have been

characterized, and adsorption isotherms have been measured for TCE. Desorption rates have been measured and models are being evaluated to rationalize the observed removal rates.

Client/Users: Consultants and educators interested in groundwater and soil remediation technology.

Detection and Assessment of Subsurface Contamination: Peter K. Kitanidis, Stanford University.

Goal: The thrust of this project is the development of better techniques for characterizing contaminated sites. Objectives include the development of better computational methods for the detection and assessment of groundwater contamination and the determination of the mechanisms and parameters which govern the transport and fate of pollutants at field scales.

Rationale: There is seldom enough information to determine with certainty the precise values of all parameters for characterizing a contaminated site, especially at the local scale. Measurements of some critical transport parameters, such as hydraulic conductivity, indicate variability over orders of magnitude over short distances. Other parameters, such as thermodynamic constants and rate coefficients, are quite variable too. In many cases, however, determination of the "effective" parameters of the heterogeneous formation, i.e., those which govern the net or "macroscopic" rate of advection, dispersion, and chemical attenuation, rather than the highly variable local rates, is sufficient and is what is sought by this study.

Approach: The developed approach combines measurements, mechanistic models describing the transport and fate of pollutants, and statistical methods. In recognition of the spatial variability of geologic formations and incomplete knowledge of their properties, the parameters which determine the transport and fate of solutes, such as conductivity, retardation, and reaction coefficients, are characterized in statistical terms. The mathematical formalism of random functions is used to describe spatially variable quantities through statistical moments, such as mean and covariance functions. These moments are obtained from data and other (such as geological) information using geostatistical techniques. Then, through the governing flow and mass transport equations, the statistics of solute concentration are determined. These methods are applied to two problems of practical interest: the evaluation of the macroscopic, or field-scale, flow and transport parameters and the conditioning of predictions on measurements.

Status: Initial efforts focused on the determination of the relation between the measurable but highly erratic local parameters and the effective parameters which govern the flow and solute transport at macroscopic scales of interest. The second year produced a numerical spectral method for carrying out computations of interest.

Client/Users: Groundwater modelers; engineers working in the characterization of hazardous-waste sites; regulators; and policy makers interested in evaluating the worth of data.

FASTCHEM Applications and Sensitivity Analysis: Peter K. Kitanidis and David L. Freyberg, Stanford University.

Goal: FASTCHEM is a collection of computer programs which can be used to predict the advection, dispersion, and geochemical transformation of chemicals emanating from utility waste disposal sites. The objectives of the work include: (1) quantifying the sensitivity and uncertainty of predicted chemical distributions (in time and space) to variations in input parameters; (2) developing a set of computer programs which apply state-of-the art estimation methods for the interpolation of parameters from sparse measurements; and (3) evaluating the literature and developing new techniques for optimal decontamination strategies at utility hazardous waste sites under uncertainty.

Rationale: Amendments to the Resource Conservation and Recovery Act in 1984 and reauthorization of the Safe Drinking Water Act in 1986 have prompted the formulation of several new regulations to protect groundwater quality. In response to new regulations and to develop a capability to assess the potential success of remedial actions, the Electric Power Research Institute (EPRI) has supported the development of the interim hydrogeochemical modeling package FASTCHEM. This package of codes can be used to simulate the advection, dispersion, and chemical attenuation of inorganic chemicals that may be leached from electric utility waste disposal sites. There is a need now to determine the applicability of the model and for incorporating subroutines for the utilization of data.

Approach: The model's sensitivity and uncertainty is evaluated through application to specific case studies. Methods for incorporating available measurements are based on linear estimation methods.

Status: The computer codes have been installed and tested and recommendations for model improvement have been made. The model has been applied to six case studies representing typical problems of ash disposal from coal-fired plants. The sensitivity of the results to the input parameters has been evaluated. An applications manual has been drafted and is currently under review.

Client/Users: The electric utility industry, regulators, and policy makers.

Dispersion Modeling of Volatile Organic Emissions from Ground-Level Treatment Systems: Lynn M. Hildemann and Paul V. Roberts, Stanford University

Goal: Treatment to remove organic substances present in contaminated groundwater can result in the emission of hazardous volatile organics into the atmosphere. This project will develop a detailed model for the dispersal of emissions from a ground-level area source into the atmosphere, with the goal of accurately predicting concentration levels near the source as well as further away.

Rationale: The potential toxicity of air emissions from waste treatment processes has been the focus of increasing concern over the past decade. However, published attempts at estimating the potential impact of such treatment processes on the local atmosphere have utilized simple dispersion models which are only reliable at significant distances downwind over long averaging times for an elevated source. A more accurate approach is needed to evaluate the risk posed in the near vicinity of a ground-level treatment process due to atmospheric emissions.

Approach: A detailed model capable of predicting the near-source dispersion of emissions from a ground-level area source will be developed. Accurate theoretical expressions for the variation of wind speed and eddy diffusivity with vertical height will be incorporated in order to accurately model dispersion in the surface layer regime. This model will be linked to an already-developed model predicting emission rates resulting from aerobic treatment of wastewaters. The model predictions then will be compared with published measurements of concentrations downwind of treatment sites.

Status: Development of the atmospheric dispersion model has been completed, and it has been linked to another model which predicts the emission rates of volatile organics based on influent concentrations and the operating conditions of the aerobic treatment unit. Currently, the predictions of the new dispersion model are being compared with those obtained using two other "popular" models under various conditions. Published experimental measurements of airborne concentrations downwind of a ground-level area source are also being sought for further testing the model's predictions.

Client/Users: Industries and regulators involved in the treatment of contaminated groundwater, and researchers concerned with assessing the risks associated with such treatment units.

CHLORINATED SOLVENTS

Oxidation of Chlorinated Solvents by Methanotrophs: Perry L. McCarty and Paul V. Roberts, Stanford University

Goal: Methanotrophic bacteria, which oxidize methane for energy, have been found capable of oxidizing chlorinated solvents such as TCE by cometabolism. The goals of this project are: (1) to evaluate the effect of competitive inhibition between methane and chlorinated compounds on the overall chlorinated solvent degradation rate; (2) to assess the importance of mass transfer limitations on treatment-reactor design; and (3) to use the knowledge gained to optimize the design for an above-ground treatment system for chlorinated solvent destruction.

Rationale: There have been several studies of treatment systems for degrading chlorinated solvents and related compounds. However, the knowledge of reaction kinetics associated with cometabolism are poorly understood so that little scientific basis currently exists for optimizing treatment reactor design. In addition, since the primary substrate, methane, the required electron acceptor, oxygen, and the chlorinated contaminants are all poorly soluble in water, mass transfer properties of treatment systems become of great significance and must be considered.

Approach: It is hypothesized that oxidation rates for methane and chlorinated contaminants can be described by a competitive inhibition model. Here, the rate-limiting step is the oxidation of either methane or TCE by methane monooxygenase (MMO). To evaluate this hypothesis, reaction coefficients for methane and TCE alone are being evaluated using a mixed methanotrophic culture derived from the Moffett Field aquifer. Reaction rates when they are used in combination are then being predicted and measured in order to test the hypothesis. In mass transfer studies, model calculations are being made for a variety of reactor configurations in order to determine flow patterns that are realistic and optimal for given treatment objectives. These calculations consider mass transfer effects and biological reaction kinetics. The model

results are expected to guide reactor design as well as help to determine important knowledge gaps that may be in need of further research.

Status: Laboratory studies have indicated basic reaction coefficients for methane and trichloroethylene utilization alone by methanotrophs. Initial studies with the two compounds together in various combinations have been conducted. Model calculations have been carried out. These studies have indicated that the presence of methane enhances rather than retards TCE degradation. Thus competitive inhibition kinetics alone does not appear appropriate in models for predicting transformation rates. The nature of this unexpected phenomenon is being explored.

Client/Users: Researchers interested in cometabolism for halogenated aliphatic compounds; and industry, consulting engineers, and state and EPA regulators who are evaluating treatment options for chlorinated solvents.

Effects of Sorption on Biodegradation of Halogenated Organics: Perry L. McCarty and Paul V. Roberts, Stanford University (funded by EPA).

Goal: The goal of this project is to determine how compound sorption onto solid surfaces such as soil and sorption media (e.g., activated carbon) affects the rates of degradation of chlorinated solvents by methanotrophic bacteria.

Rationale: Rates of biodegradation of organic compounds are known to be affected by sorption onto surfaces, but the nature of this effect is not well understood. Whether it enhances or reduces transformation rates appears to depend upon properties of the sorbed compound, the surface to which it is sorbed, and the biological process involved. Greater knowledge of the effect of sorption is needed in order to better predict fate of chemicals in the environment, and to devise treatment schemes where sorption is involved.

Approach: The availability of sorbed trichloroethylene (TCE) to biological degradation by methanotrophic bacteria, which use methane as primary substrate for growth, is being evaluated. First, biotransformation kinetics for oxidation of TCE by non-fed (resting) methanotrophic bacteria are being determined, using a mixed culture derived from the Moffett Field site, and parameters associated with sorption kinetics of TCE on a well-defined synthetic media (silicalite) as well as aquifer solids are being determined. A numerical model is also being developed to relate desorption and biotransformation kinetics, using the hypothesis that transformation rates are directly related to solution concentration of TCE. In addition, transformation rates of chloroform (CF), in the presence and absence of TCE, are being conducted.

Status: Studies of the kinetics of TCE and CF transformation by resting cells and the effect of sorption on TCE transformation rates have been completed. Four manuscripts resulting from this work have been published, and two more are under review. Significant findings of this research are that TCE transformation products are toxic to methanotrophic bacteria, and that resting cells have a finite capacity for TCE and CF transformation. A new cometabolic transformation model was developed that incorporates the phenomena of Monod transformation kinetics, product toxicity, competitive inhibition, and transformation capacity. A model for a

two-stage treatment system comprised of a growth reactor and a transformation reactor was developed.

Client/Users: Researchers interested in cometabolism for halogenated aliphatic compounds; and industry, consulting engineers, and state and EPA regulators who are evaluating treatment options for chlorinated solvents.

Long-Term Chemical Transformation of 1,1,1-Trichloroethane (TCA) and Freon 113 Under Aquifer Conditions: Martin Reinhard, Stanford University

Goal: The goals of this project are to (1) determine the rates and pathways of chemical transformation of 1,1,1-trichloroethane (TCA) and Freon 113 under conditions representative of those encountered in an aerobic aquifer, and (2) determine the extent to which sorbing aquifer materials and different solution composition may influence transformation rates and pathways.

Rationale: Previous data obtained at high temperature have demonstrated that TCA undergoes abiotic dehalogenation in aqueous solution. However, extrapolation to groundwater temperature is fraught with uncertainty, and the influences exerted by the presence of aquifer solids and groundwater solutes are not well understood.

Approach: This work involves a long-term (5-year) study of the rates and pathways of reaction of TCA and Freon 113 in aqueous solution in the presence, as well as in the absence of aquifer material. Because under ambient conditions, the half-life of TCA is on the order of a year and several different products may form, substrate disappearance and product formation will be monitored over several years in order to obtain mass balances.

Status: The test systems have been in operation for 22 months, and several products of TCA transformation, including 1,1-dichloroethylene, have been detected and quantified. The study is expected to be completed in 1994.

Client/Users: Consultants, regulators, and researchers interested in natural processes affecting the long-term fate of TCA and Freon 113 in the subsurface environment.

Use of Starvation and Stress Promoters for Biodegradation of Hazardous Wastes: Abdul Matin, Dunja Grbić -Galić , Stanford University

Goal: The goal of this project is to use bacterial-stress (especially starvation) promoters to create recombinant strains that exhibit high biodegradative activities under typical environmental stress conditions.

Rationale: Microbial degradative activities in the environment can be limited by stresses such as nutrient deficiencies for carbon, nitrogen, or phosphorus. Bacterial strains that are capable of high degradative activities under such environmental stresses should be useful in the remediation of hazardous waste sites.

Approach: Stress promoters are genetic elements that are activated in response to specific stress conditions. Bacterial promoters that are switched on under carbon starvation have been isolated

and characterized. Our approach is to splice the toluene-4-monooxygenase (T-4-MO) gene which degrades hazardous compounds such as trichloroethylene (TCE), under the regulation of these promoters and to characterize the degradative activities of the resultant strains.

Status: T-4-MO has been placed under the regulation of two carbon starvation promoters and under a more generalized stress promoter in *E. coli*. Experiments have begun to characterize these constructs. Attempts are being made to optimize the regulation of one of the carbon starvation promoters by removing intervening DNA sequences between the promoter and T-4-MO. Organisms with the more generalized stress promoter are able to maintain TCE degradative activity for several hours after the onset of starvation.

Client/Users: Researchers, consultants, and regulators interested in understanding the process of biotransformation at a fundamental level and in applying this understanding to the improvement of biotransformation rates.

Subsurface Mixing of Nutrients and Groundwater for in-Situ Bioremediation: P. L. McCarty, P. K. Kitanidis, P. V. Roberts, and L. Semprini, Stanford University

Goal: In-situ bioremediation of groundwater generally requires that gaseous substances such as methane and oxygen be mixed with contaminated groundwater. A scheme by which the gases are introduced directly into the groundwater for mixing with the contaminants is proposed for evaluation in order to avoid bringing contaminants to the surface for this purpose.

Rationale: In-situ bioremediation of chlorinated solvents in groundwater with methanotrophic bacteria requires that the primary substrate, methane, and oxygen for its oxidation be introduced into the groundwater and mixed with the contaminants. This is difficult to accomplish, especially when the contaminants do not sorb strongly to the soil. Bringing contaminated groundwater to the surface for this purpose poses a health hazard, and so a method for accomplishing the introduction and mixing of gases without removing groundwater is desirable.

Approach: A subsurface mixing system is proposed which consists of a series of submerged wells with intake screens at the bottom and top. A pump permits drawing groundwater into the well through the bottom screen and pumping it back into the aquifer through the top screen, or vice versa. In the well oxygen and methane are introduced and mixed with the groundwater. An analysis is being conducted to determine the effect of well depth, well placement, and pumping rate and direction on the degree of mixing of dissolved gases with contaminated groundwater, and to predict the effect of these operating parameters on the degree of in-situ bioremediation that can be achieved. Alternative methods for introduction of gases into the submerged wells are also being evaluated.

Status: This project began in October 1990. A combined analytical and numerical model for mixing has been developed and is being used for the design of the pilot study proposed for the St. Joseph, Michigan, Superfund site. In a parallel study, the growth of microorganisms along stream tubes, the recycle of nutrients to a single, submerged mixing unit, and the treatment of chlorinated solvents with time are being calculated numerically.

Client/Users: Researchers studying in-situ bioremediation; and state and EPA regulators, industries, and consulting engineers with interests in biotreatment systems for organically contaminated groundwaters.

Test-Bed Evaluation of in-Situ Bioremediation of Chlorinated Aliphatic Compounds by Toluene: P. L. McCarty, P. V. Roberts, L. Semprini, and G. Hopkins, Stanford University

Goal: The goal of this project is to evaluate in the field the rate and extent of degradation of chlorinated aliphatic compounds through cometabolism using phenol as a primary substrate.

Rationale: Recent research has indicated that microorganisms containing the toluene monooxygenase (TMO) or toluene dioxygenase (TDO) enzyme can oxidize chlorinated aliphatic compounds such as trichloroethylene (TCE) by cometabolism, similar to biodegradation by methanotrophs with methane monooxygenase (MMO). The toluene oxygenases can be induced by several primary substrates, including phenol. In order to obtain a comparison between the relative advantages and disadvantages of the TMO or TDO systems and the MMO enzyme system, an evaluation will be conducted at the field site at Moffett Field Naval Air Station in California. A four-year evaluation of the MMO system has already been completed here.

Approach: The field study will be conducted in the same manner as the previous study in which methane was used as a primary substrate so that the results can be directly compared. Here phenol and oxygen will be dissolved in recycled groundwater along with TCE, dichloroethylene (DCE), and vinyl chloride (VC) for introduction into a confined aquifer about 4 m below the surface that is about 1.2 m deep and 6 m long. The growth of a native phenol-degrading population, and the rate and extent to which the introduced chlorinated compounds are removed will be continuously monitored by automatic extraction of groundwater from monitoring wells and on-site analysis. The extent of transformation will be evaluated through comparison of concentration decreases with conservative tracers.

Status: Funds to begin this two-year study were received in October 1990. Laboratory-scale bioreactors were used to evaluate the relative performance in chlorinated aliphatic transformation by methane, phenol, toluene, and ammonia-oxidizing bacteria. Toluene and phenol were equivalent in performance, but different from that by methane, and much better by some compounds. The first season of field testing with phenol injection to determine effectiveness with TCE, cis-DCE, and trans-DCE transformation is now complete with results that are consistent with the laboratory-scale studies. Effective transformation of TCE and cis-DCE was achieved, but trans-DCE transformation was limited. A report on these results is in preparation, and a plan for the second year of study is under review.

Client/Users: State and EPA regulators, industries, and consulting engineers concerned with chlorinated solvents and related compounds present in groundwaters.

Demonstration of in-Situ Bioremediation of Chlorinated Aliphatics by Methanotrophs at St. Joseph: P. L. McCarty, P. V. Roberts, S. M. Gorelick, P. K. Kitanidis, and L. Semprini, Stanford University

Goal: Laboratory and field studies recently completed at Stanford University demonstrated that in-situ cometabolic biodegradation of chlorinated solvents and related compounds by methanotrophic bacteria is feasible. This project is for the evaluation of alternative technologies and design of a system for conducting such treatment at full scale.

Rationale: Bioremediation of groundwaters offers great promise because it results in destruction of contaminants. However, application of promising techniques requires research and demonstration at full scale. Field and laboratory studies have helped develop a basic understanding of the processes involved in methanotrophic treatment of chlorinated aliphatic compounds; the next step toward application is an evaluation of potential technologies for the process through research and demonstration at full scale.

Approach: The St. Joseph, Michigan, Superfund site has contamination of a relatively homogeneous fine-sand aquifer with mg/L concentrations of trichloroethylene, dichloroethylene, and vinyl chloride. Laboratory, field, and modeling studies conducted by the WRHSRC indicated that conditions were ideal for evaluating in-situ bioremediation at this site. In order to develop an appropriate treatment system design, additional site characterization is required, alternative technologies need to be researched, modeling studies for alternatives need to be evaluated, and a system design needs to be developed for evaluation by the responsible industries, their engineers, and state and EPA regulators. These tasks will be carried out by a team of researchers at Stanford University in cooperation with the interested parties.

Status: Initial funding for this two-year study was received from EPA and the Gas Research Institute in September 1990. Model development has been completed and design for the St. Joseph pilot study are nearing completion. Detailed characterization of the site has been completed in a cooperative study by the industry involved and the EPA Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma. These results will be used to locate the pilot system. Laboratory studies for a methane and oxygen to groundwater transfer system are underway.

Client/Users: State and EPA regulators, industries with halogenated solvent groundwater problems, and consulting engineers responsible for design of treatment systems to remove and perhaps degrade chlorinated solvents and related compounds present in groundwaters.

Determining and Modeling Diffusion-Limited Sorption and Desorption Rates of Organic Contaminants in Heterogeneous Soils: Paul V. Roberts, Stanford University

Goal: The overall goal of this project is to advance the understanding of the basic processes governing the uptake and release of aqueous-phase organic contaminants in a heterogeneous porous medium.

Rationale: Aquifer remediation strategies, such as pump-and-treat or bioremediation, can be greatly prolonged by the diffusion limitations on sorption and desorption from the soil matrix. Equilibrium models, which are the most commonly used solute transport models, do not account for these effects. There is presently little basis for assessing when mass transfer conditions are favorable for pump-and-treat and/or bioremediation strategies, nor is there an accepted method for predicting the required duration of remediation efforts.

Approach: Long-term batch experiments for measuring the uptake and release rates of several contaminants from solids obtained from an experimental aquifer restoration site have been conducted. The data are used to evaluate and parameterize existing transport models.

Status: A purge-and-trap method for studying desorption rates has been developed that enables the conduct of long-term experiments; mass balances confirm the efficacy of the experimental method. Batch sorption rate data have been interpreted within the framework of a pore-diffusion model that simulates either sorption or desorption. A mathematical model has been developed to interpret the rate data, permitting estimation of the effective diffusivity; either linear or Freundlich isotherm data can be accommodated. Desorption rate behavior conforms to the grain-scale mathematical model. Application of the laboratory-determined parameters as inputs to a transport model simulates the transport behavior at the Moffett Field site, more successfully than does an equilibrium model. Work is continuing on diffusion into clay layers and on temperature effects. WRHSRC funding for this topic terminates in February 1992.

Client/Users: Researchers interested in the effect of mass transfer limitations on the transport or biodegradation of organic contaminants; and state and EPA regulators, industry, and consultants concerned with site remediation.

AROMATICS

Interactions between Electron Acceptors in the Treatment of Wastewaters Containing Sulfate, Chlorophenols and Acetate: Sandra L. Woods, Oregon State University

Goal: The goal is to develop and verify a mathematical model for anaerobic biotransformations in the presence of competing electron acceptors, and to measure process kinetic constants. Electron acceptor interactions between chlorophenols and their dechlorinated metabolites and interactions between chlorophenols and sulfate are examined.

Rationale: Reductive dechlorination of chlorinated aromatic compounds appears to progress such that parent compounds are almost completely removed before degradation of metabolic products begins. To evaluate this hypothesis, the kinetics of pentachlorophenol biotransformation is evaluated in the presence of varying quantities of alternate electron acceptors (metabolic products and sulfate).

Approach: Organisms acclimated to pentachlorophenol, or pentachlorophenol and sulfate, are grown in continuous-flow anaerobic reactors. The reactors are allowed to reach steady state and then used as a source of organisms for subsequent batch experiments. Progress curves for chlorophenol, sulfate, and acetate degradation are generated from the batch experiments. From the results the effect of alternate electron acceptors on the rate of chlorophenol biotransformation are determined.

Status: With acclimation pentachlorophenol is biotransformed by concurrent reductive dechlorination reactions occurring at the ortho, meta, and para positions. Each of the three possible tetrachlorophenols appears as an intermediate, as well as four trichlorophenols and three dichlorophenols. The rate of reductive dechlorination is fastest for the more highly chlorinated congeners. Although reductive dechlorination at the ortho position is observed most frequently, para dechlorination is often more rapid. Additional studies have shown the dependence of reductive dechlorination rates on the apparent oxidation/reduction potential of the system. Rates increase with decreasing oxidation/reduction potential, and reductive dechlorination of pentachlorophenol has been shown to occur at high sulfate concentrations when the oxidation/reduction potential is controlled.

Client/Users: Consultants and regulators concerned with site characterization for bioremediation or above-ground biological treatment of pentachlorophenol, and researchers interested in biotransformation reaction kinetics in a complex system.

Enhancing Biodegradation with Sorption and Alternating Aerobic/Anaerobic Environments: Kenneth J. Williamson, Peter O. Nelson, Oregon State University

Goal: The goal is to develop and verify a mass transport and biokinetics model of the sorption and biological degradation of pentachlorophenol and its degradative products by anaerobic and aerobic biofilms on activated carbon.

Rationale: Granular activated carbon (GAC) has been shown useful for enhancing biological treatment of toxic organic compounds by adsorption, resulting in reduced aqueous

concentrations to below inhibitory levels. This enables biological degradation to occur of toxic compounds by the attached biofilms. Haloaromatic compounds undergo different biodegradation pathways under anaerobic and aerobic conditions. Anaerobic pathways typically result in metabolic products that cannot undergo further metabolism in that environment. By sorbing these compounds to GAC and then moving the GAC to an aerobic environment, complete and rapid degradation may be possible.

Approach: Anaerobic and aerobic biofilms will be developed on GAC maintained in upflow expanded beds with liquid recycle. Acetate will be used as the electron donor for the anaerobic reactor and the primary electron donor for the aerobic reactor. Pentachlorophenol will be fed to the anaerobic column, and should rapidly dechlorinate to a series of tri- and di-chlorophenols. These metabolic products should sorb strongly to the GAC. The GAC will be moved from the anaerobic column to the aerobic column with a solids retention time of 30 days. The tri- and di-chlorophenols slowly desorb in the aerobic reactor and should undergo degradation by the aerobic biofilms.

Status: Experiments have been conducted to determine the degradation rates of pentachlorophenol and its degradative products under aerobic and anaerobic conditions. Adsorption isotherms and rates of adsorption and desorption have been determined for these same compounds. Near steady-state removals of pentachlorophenol and its metabolic products have been determined in the anaerobic and aerobic GAC columns under the 30-day solids retention time and 3-day hydraulic detention times in both the anaerobic and aerobic columns. Data collection is continuing as the columns approach steady-state conditions.

Client/Users: Researchers and consulting engineers interested in developing innovative biological treatment technologies for chlorinated compounds using activated carbon.

Development and Verification of a Numerical Model to Predict the Fate and Transport of Chlorinated Phenols in Groundwater: Jonathan D. Istok and Sandra L. Woods, Oregon State University

Goal: The objectives are to develop a numerical model to predict the fate and transport of pentachlorophenol and its primary anaerobic degradation products in field soils and groundwater aquifers, and to verify the model using laboratory and field experiments.

Rationale: Predictive models of pollutant transport are needed for site characterization and to design effective biological remediation strategies.

Approach: A mathematical model was developed based on the processes of advection, dispersion, diffusion, sorption, and anaerobic degradation for pentachlorophenol and its metabolites, an electron donor (acetate), and biomass. Monod kinetics and a "macroscopic bulk concentration" concept are used to describe degradation and growth. The resulting set of nonlinear differential equations are solved by the finite-difference method. Experiments are conducted using a Chehalis soil in batch reactors, columns, and in large soil tanks consisting of an aluminum box (2 m wide by 4 m long by 20 cm deep) supported by a steel framework. Dispersion coefficients and sorption parameters were measured in miscible displacement experiments in packed soil columns (30.0 cm long by 5.38 cm in diameter). Comparisons

between predicted and measured effluent concentrations will be made during miscible displacement experiments in inoculated soil columns.

Status: A complete set of batch and column experiments have been completed. Fate and transport parameters obtained from these experiments are being used to simulate PCP transport under a wide range of field conditions. The simulations are also being used to design column validation experiments.

Client/Users: Consultants and regulatory agencies concerned with site characterization for bioremediation and understanding of pentachlorophenol fate and transport.

Anaerobic Microbial Transformation of Homocyclic and Heterocyclic Polynuclear Aromatic Hydrocarbons: Dunja Grbić -Galić , Stanford University

Goal: Monoaromatic hydrocarbons, such as toluene and benzene, have been shown to undergo microbial degradation in the absence of oxygen, and even to serve as microbial growth substrates under those conditions. However, reports on anaerobic biodegradability of polynuclear aromatic hydrocarbons (PAH) are scarce. The goal of this project is to seek anaerobic microbial activity toward PAH and complex nitrogen, sulfur, and oxygen heterocycles (NSO) under sulfate-reducing and methanogenic conditions. The primary emphasis is on evaluation of biotransformation routes once the activity is established.

Rationale: PAH and NSO are chemically stable; some of them are potential carcinogens. They are widespread environmental contaminants. Frequently, oxygen is not present in the contaminated habitats, so that the anaerobic transformation is the only possibility for detoxification or destruction of these compounds. Thus, it is important to know whether such transformations can occur, and if so, what are the microbial physiological groups involved, what is the degree of transformation, what intermediates and products are formed, and what interactions occur in mixtures of PAH and NSO.

Approach: Saturated batch microcosms with aquifer solids from the anoxic zone of the Pensacola, Florida, creosote-contaminated aquifer have been amended with defined prerduced mineral medium, and with either single PAH (indene, naphthalene, acenaphthene) and NSO compounds (indole, quinoline, isoquinoline, benzothiphenene, benzofuran), or with mixtures of some of these chemicals. In some cases lactate, benzoate, or mixtures of benzoate and fatty acids have been added to examine the possibility of cometabolic transformation. In some microcosms, sulfate has been added as a potential electron acceptor. Once transformations are observed, attempts of culture enrichment and isolation will be started. In addition to aquifer-derived microcosms, mixed methanogenic cultures (originally obtained from sewage sludge), shown to degrade toluene, benzene, naphthalene, and acenaphthene, will be evaluated.

Status: Indene, naphthalene, indole, quinoline, isoquinoline, benzothiphenene, and benzofuran have been completely degraded (to CO₂ and CH₄) as single substrates under methanogenic conditions, within 1-2 months of incubation at 35°C. With quinoline and isoquinoline, transformation intermediates have been detected. Degradation occurred when the compounds were present as sole carbon and energy sources, but degradation was accelerated in the presence of additional organic substrates (benzoate, fatty acids). In addition, transformation of acenaphthene (a PAH) to 1-acenaphthenol and quinoline to 2-quinolinol have been observed under sulfate-reducing conditions. Further degradation of 2-quinolinol to unknown products has also been noted. The sulfate reduction occurs concomitant with acenaphthene and quinoline transformation, and these transformations are dependent on sulfate reduction (and vice versa), indicating participation of sulfate reducers in the degradation process. The sulfate-reduction process is being studied further. Efforts in enrichment and isolation of cultures from the microcosms are being continued.

Client/Users: EPA regulators, industries, and consultants concerned with clean-up of sites contaminated by petroleum or creosote.

PAH Degradation by Methanotrophic Bacteria: Perry L. McCarty and Dunja Grbić - Galić , Stanford University

Goals: Polycyclic aromatic hydrocarbons (PAHs) are hazardous compounds found associated with wood preservatives (creosote), coal gasification sites, and petroleum product wastes. The goal of this project is to explore the ability of a methanotrophic mixed culture developed at Stanford to initiate the oxidation of four characteristic PAHs, thereby rendering the compounds more susceptible to further degradation by other microorganisms.

Rationale: The compounds being studied are naphthalene, phenanthrene, pyrene, and benzo(a)pyrene, which increase in complexity from two to five rings. The initial step in oxidation of PAHs generally involves the activities of monooxygenases or dioxygenases. The methane monooxygenase (MMO) present in methanotrophs is quite nonspecific and so offers the potential for initiating PAH oxidation. The Stanford mixed culture has been well characterized and is being used for studies of chlorinated solvent degradation, and possesses the soluble MMO which is believed to be the form with broad substrate specificity.

Approach: The initial step is to evaluate the ability of the methanotrophic culture to initiate oxidation of the four PAHs. HPLC is being used to measure the concentration of the four compounds and to detect intermediates in PAH oxidation. Initially, the four compounds will be added individually to aqueous solutions containing growth nutrients for the methanotrophs, a culture (about 250 mg/L) will be added, and the change in concentration of the PAH with time will be monitored. If transformation indeed occurs, then a broader study will be initiated to determine the effect of sorption to soil on PAH oxidation by methanotrophs. At that time, ¹⁴C-labeled PAHs will be used to make better mass balances because of the analytical difficulties in making mass balances when soils are used. If oxidation is obtained, then the study will be broadened to evaluate rates and extents of transformations of soil bound PAH by methanotrophic bacteria.

Status: This one-year exploratory project was started in July 1991. The rapid oxidation of naphthalene to naphthanol within a few hours has been determined. The other three PAHs are poorly soluble in water and also sorb strongly to bacterial cells so that quantification of results is more difficult. Procedures for better quantification are under development.

Client/Users: Industry and regulatory authorities concerned with PAH contamination of soil from creosote sites and sites where consumer gas was produced.

In-Situ Biological Treatment of Aromatics in Groundwater: Martin Reinhard and Perry L. McCarty, Stanford University

Goal: The objective of this study is to develop and characterize microbial consortia capable of transforming aromatic hydrocarbon compounds under anaerobic conditions with emphasis on methanogenic, sulfate- and nitrate-reducing conditions, and to understand the effect of environmental factors on the transformation processes.

Rationale: Although most gasoline constituents are readily degraded in aerobic surface water systems, the groundwater environment associated with hydrocarbon spills is typically anaerobic,

thus precluding aerobic degradation pathways. In the absence of oxygen, degradation of gasoline components can take place only with the utilization of alternate electron acceptors such as nitrate, sulfate, carbon dioxide, and possibly ferric iron or some other metal oxides. Neither the potential for transformation of these compounds under field conditions using alternate electron acceptors, nor the rate of such transformations has yet been assessed.

Approach: Microbial consortia from aquifer solids and other sources are being enriched for anaerobic biotransformation of benzene and selected alkyl-substituted monoaromatic compounds. The different media for the enrichments are formulated to favor consortia that use selected electron acceptors (nitrate, sulfate, and carbon dioxide), and mixtures of aromatic compounds are being used to ascertain multicomponent effects on acclimation. Fundamental kinetic constants of the individual microbial consortia will be determined using substrate utilization and biological growth experiments. Results of laboratory studies will be compared with degradation rates determined in bioreactors placed into a gasoline-contaminated aquifer at the Seal Beach site in Southern California. The field research is being developed and carried out in cooperation with research staff of the Orange County Water District (Dr. Harry F. Ridgway and Don Phipps).

Status: Laboratory studies with ^{14}C -labeled compounds confirmed that toluene oxidation under sulfate-reducing conditions occurs. The hydrodynamic characteristics of the three in-situ bioreactors at Seal Beach have been determined and experiments are underway to assess biotransformation rates under prevailing anaerobic conditions. Different redox regimes have been induced at the field site, and contaminant removal is being assessed. Toluene and m,p-xylene removals occurred without adaptation time, along with nitrate removal. The possibility of biodegradation associated with slower observed removals of benzene and o-xylene needs to be confirmed.

Client/Users: Researchers interested in anaerobic biotransformation of hydrocarbons and aquifer bioremediation; and state and EPA regulators and industry concerned with gasoline and hydrocarbon remediation.

Biotransformation of Ordnance Wastes Using Unique Consortia of Anaerobic Bacteria: A. Morrie Craig and Sandra Woods, Oregon State University

Goals: The objectives are to determine trinitrotoluene (TNT) degradation rates and transformation products with anaerobic metabolism by sheep ruminal microorganisms utilizing ^{14}C radiolabel.

Rationale: Pilot trials have shown that a new source of bacteria capable of degrading aromatic compounds has been found in sheep's rumen. The uniqueness of these microorganisms is the time rate in which total degradation of the toxic molecules occur. Few anaerobes from sediments can degrade TNT; however, preliminary evidence has shown that sheep microorganisms can degrade 100 mg/mL within 96 hours. Commercializations of these bacteria in bioremediation of munitions sites for the Navy and other branches of the armed forces would be highly desirable.

Approach: A three-fold approach will be used: 1) the ruminal microorganisms will be enriched for TNT degradation, and a partially purified bacterial consortium will be defined; 2) degradation of radiolabeled TNT will be used to identify the metabolic transition and end products of TNT metabolism; and 3) optimum growth parameters and degradation rates utilizing this consortium will be determined.

Status: Primary cultures are currently degrading TNT within 96 hours. Different select media are being tried to enhance growth of detoxifying organisms and degradation rates. Radiolabeled trinitrotoluene (TNT) has been incubated with ovine rumen fluid which has been determined to biotransform the TNT into triaminotoluenes and other products yet to be determined.

Client/Users: The U.S. Navy and other DOD units, their consultants, and regulatory agencies who are interested in the biotransformation of munitions; and researchers who are exploring new microbial consortia for aromatic compound degradation.

Aerobic Methanotrophic Transformation of Biphenyl, Monochlorobiphenyls, and Dichlorobiphenyls: Dunja Grbić -Galić , Stanford University

Goal: Polychlorinated biphenyls (PCBs) with a low degree of chlorination (mono- and dichlorobiphenyls [MCB and DCB]) have been demonstrated to undergo aerobic transformation by pseudomonads and related heterotrophic aerobic bacteria. However, ortho-chlorinated congeners usually represent an obstacle for degradation. The goal of this project is to take advantage of degradative capabilities of a different group of aerobic bacteria, methanotrophs, by using methanotrophic pure and mixed microbial cultures shown to transform trichloroethylene (TCE). The PCB congeners of interest are ortho-chlorinated 1-MCB and 4-MCB, and 2,3-, 2,6-, 2,2'-, and 2,4'-DCB.

Rationale: MCB and DCB (often ortho-chlorinated congeners) have been shown to accumulate as products of anaerobic transformation (reductive dechlorination) of industrial PCB mixtures (Aroclors) and single highly chlorinated congeners. Because of the lower oxidation-reduction potential of the less chlorinated congeners (relative to congeners with a high degree of chlorination), aerobic microorganisms that use oxygen as an electron acceptor and as a reactant for oxygenation reactions would be the microorganisms of choice for degradation of MCB and DCB. Methanotrophs, the microorganisms which grow on methane and a small number of other C₁-compounds, have a suitable oxygenative enzyme (methane monooxygenase [MMO]) with a very relaxed substrate specificity, and might be able to oxidize biphenyl, MCB, and DCB. So far, methanotrophs have not been tested as degraders of PCBs, although they have been demonstrated to cometabolize a broad range of other organic pollutants, including aromatics, aliphatics, heterocycles, and chlorinated compounds.

Approach: Mixed and pure methanotrophic cultures developed in the Stanford laboratory are being tested for their capability to cometabolize biphenyl, MCB, DCB, and hydroxylated biphenyls. Experimental work will be initiated with mixed and pure methanotrophic cultures (mixed culture MM2 and pure culture *Methylomonas* sp. strain MM2, both TCE-degraders isolated from the Moffett Field groundwater aquifer) as potential cometabolizers of ortho-MCB and DCB. The cultures will be daily supplemented with methane throughout the incubation

period with PCBs. The culture fluids will be sampled after 20 days of incubation, samples will be extracted and processed, and analyzed spectrophotometrically for transformation products.

Status: Mixed culture MM2 transformed biphenyl, 2-MCB, 2,4-DCB, 2,4'-DCB, 2,2'-DCB, 2,3-DCB, and 3-chloro-2-hydroxy-B (3-C-2-BPOL). 2-MCB was converted to a yellow product and an acid-extractable metabolite, identified as a hydroxylated derivative of 2-MCB. From GS/MS patterns it is inferred that the hydroxy-substituent was added to the chlorinated, rather than the nonchlorinated ring. Additionally, a ¹H-NMR spectrum (in CDCl₃) from the total extract revealed the presence of a mononuclear aromatic, and a C₂-aliphatic compound. 2,4-DCB was converted by culture MM1 to a yellow product and an acid-extractable product, whereas 2,4'-DCB was transformed to a water-soluble yellow product, as was 3-C-2-BPOL. *Methylomonas* sp. MM2 transformed biphenyl, 2-MCB, 4-MCB, 2,4-DCB, 2,3-DCB, 3-C-2-BPOL, and 2-C-4-BPOL, with formation of yellow and/or acid-extractable products. The characterization and identification of some of these products is in progress.

Client/Users: The results of this project should be important to EPA and to industries concerned with PCB removal from the contaminated sites.

HEAVY METALS

Trace Metal Removal Processes: James O. Leckie, Stanford University

Goal: The goal is development of an experimental data base and mathematical model for mass-transfer-limited adsorption of trace metals in porous particles. Experimental results and the mathematical model will facilitate the design of a removal process utilizing porous metal oxide particles.

Rationale: Previous experimental work with porous, high-surface-area oxide particles has demonstrated a dramatic increase in adsorption capacity of the porous material relative to nonporous particles. From an engineering perspective, porous particles with high internal surface area are appropriate for treating large volumes of dilute metal-bearing wastewaters and allowing regeneration and recycling of the adsorbent. Reactions within porous particles can be severely limited by intraparticle diffusion. Investigation of diffusional limitations is an objective of this project. Choice of particles with a suitable pore size distribution will provide the high surface area desired without imposing severe pore diffusion limitations.

Approach: The approach involves the design and implementation of a parametric study of adsorption of an oxyanion (selenite) and a cation (cadmium) on porous, amorphous alumina particles. Samples of three different porous aluminum oxide particles were obtained from ALCOA for the study. The first phase of the experimental work involves the physical-chemical characterization of the adsorbent (particle morphology, particle size distribution, pore size distribution, surface area, solid structure, surface site density, acidity constants, electrolyte-binding constants, and trace-element-binding constants). The second and main phase of the experimental work explores the role of mass transfer on trace element adsorption in the porous alumina particles. The parametric study includes experiments at variable pH values, solid and trace element concentrations, solid/solution ratios, and ionic strengths. Based on particle characterization and data developed in the second experimental phase, a diffusion model will be used to test the hypothesis of diffusion limited adsorption.

Status: The physical-chemical characterization of the adsorbent has been completed. Equilibrium experiments with selenite and cadmium have confirmed the high adsorptive capacity of the porous alumina. Rate experiments with cadmium and selenite indicate that the approach to equilibrium depends on particle size and solid structure (porosity, tortuosity) as expected for diffusion-limited adsorption. Equilibrium data were modeled with the triple-layer surface complexation model and the results are satisfactory considering the wide range of solid/solution ratios. The rate of uptake experiments were modeled assuming diffusion of solute in a sphere from limited volume. The last phase of the project will be focused on model refinement.

Client/Users: Researchers interested in trace metal removal processes; electronics, electroplating, and power industries; areas with high trace metal concentration problems (e.g., Kesterson reservoir).

Hexavalent Chromium Sorption and Desorption in Natural Soils and Subsoils: Peter O. Nelson and Jonathan D. Istok, Oregon State University

Goal: The intent of this research is to gain a better understanding of the chemical behavior of hexavalent chromium, Cr(VI), in natural soils. Emphasis will be placed on determination of reaction kinetics and the effects of competing solute anions on Cr(VI) sorption and desorption. Results will be used to improve transport modeling of the fate of Cr(VI) and to better design remediation schemes for chromium-contaminated soils.

Rationale: Remediation schemes for chromium-contaminated sites give strong consideration to soil flushing, or pump-and-treat technology. Pump-and-treat has been selected for at least one Region 10 site (United Chrome Products), and is being considered for many others around the country. The efficacy of pump-and-treat is highly dependent on chromium sorption and desorption kinetics and on the influence of competing solute anions. Models to predict the transport of Cr(VI) in soils must therefore incorporate these effects.

Approach: A controlled laboratory investigation is proposed in which Cr(VI) sorption and desorption reactions with natural soils and subsoils are studied. Batch reactor experiments will be used to determine equilibrium sorption parameters for chromate and sorbing cosolutes on soil and to study sorption and desorption kinetics over extended time periods (weeks to months) that are relevant to soil contamination sites. Soil column studies will be used to more closely simulate field conditions of porous media flow for investigation of diffusion-limited sorption and desorption kinetics. This latter is necessary for transport modeling and the preliminary design of in-situ chemical extraction- remediation processes.

Status: Batch adsorption experiments indicate that Cr(VI) removal in uncontaminated soil approaches equilibrium after 120-hours reaction time. Reduction of Cr(VI) to Cr(III) and subsequent precipitation/adsorption is a concomitant removal process. The reduction reaction appears to be coupled with the presence of magnetite in the soil. A surface complexation model successfully predicts equilibrium Cr(VI) adsorption in which both CrO_4^{2-} and HCrO_4^- are the sorbing species. Competitive sorption from a suite of oxyanions is being investigated. Soil column experiments have thus far investigated the empirical desorption rate of Cr(VI) in contaminated soil using extraction solutions containing competitive oxyanions. Rate of Cr(VI) desorption is decreased by the presence of a NaCl background electrolyte relative to that in distilled water. Of the competing oxyanions, the order of effectiveness for enhancing Cr(VI) desorption is: $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$.

Client/Users: Practitioners selecting remediation processes for sites with hexavalent chromium contamination will benefit from the methodology developed in this research.

TRAINING AND TECHNOLOGY TRANSFER PROJECT DESCRIPTIONS

Hazardous Waste Training: Kenneth J. Williamson, Oregon State University, and Gilbert Albelo, Mt. Hood Community College

Goal: The goal is to develop a comprehensive and coordinated program of hazardous substance training in the state of Oregon involving the community colleges.

Rationale: A coordinated training program is not available in Oregon to train individuals for careers in the hazardous substance field.

Approach: A consortium of higher-education, regulatory, and industrial representatives was developed to plan a multiple-level curriculum for hazardous substance management.

Status: A curriculum has been developed and initiated at four community colleges. The four levels include an 8-hour course for small quantity generators, a 40-hour course for hazardous material handlers and emergency responders, a one-year curriculum for hazardous material technicians, and a two-year Associate Arts degree in hazardous materials management. The project is completed.

Advanced Topic Workshops: Lewis Semprini, Stanford University

Goal: The goal is to give advanced topic workshops to transfer results of basic and applied research being performed at the Center to regulators, consultants, industry, and researchers, illustrating how the research findings pertain to problems encountered in practice.

Rationale: There is an expressed need among the community working on hazardous substance problems for the most recent available research findings in the field together with a theoretical foundation on which the research findings are based.

Approach: The Center is presenting these workshops primarily in California where the expressed need has been the greatest. They are being provided in conjunction with the University of California Extension Program in Environmental Hazard Management to complement the basic training program which they already provide. The one- to two-day workshops are presented by a group of Center researchers to provide a broad range of expertise on central contaminant problems of concern in EPA Regions 9 and 10.

Status: The workshop entitled "Biological Transformations of Chlorinated Solvents in Subsurface Systems—Natural Processes and In-Situ Bioremediation" was given in Pasadena on October 24, 1991. The workshop was attended by 70 professionals from industry, governmental agencies, and consulting firms. This workshop was previously given in Portland, Stanford, and Irvine. It is planned to give the workshop in the Seattle area in the future. Several 3- to 4-day workshops have been proposed by Center faculty on computer modeling related to groundwater problems, and may be available in the coming year. In addition a one-day course on "Advanced Analytical Methods for Organics" will be given at the HAZCOM conference in Long Beach, California, in April, 1992.

Continuing Education Program: Kenneth J. Williamson, Oregon State University

Goal: The goal of this activity is to provide a series of continuing education courses about hazardous substance management to non-degree students.

Rationale: A need exists by regulators, consultants, and industrial personnel who are presently employed in the hazardous substance management to obtain greater knowledge and education related to their field. Continuing education courses can provide fundamental educational needs that are not met by conferences, seminars, and workshops alone.

Approach: A series of extension courses has been developed by the Oregon State University WRHSRC faculty, to be given at the Tektronix Learning Center, Beaverton, Oregon, which is near the Portland area, where the need is great.

Status: A six-course sequence has been developed to be offered on a two-year cycle in the Portland area. The courses cover fundamentals of hazardous substance management and chemistry, legislation, fate and transport, waste minimization, and groundwater remediation. Enrollment averages about 20 persons in each course. A certificate of completion is given all persons who complete the six courses. This project is completed.

Conference Sponsorship: Kenneth J. Williamson, Oregon State University, and Lewis Semprini, Stanford University

Goal: The goal is for the Center to actively participate in the cosponsorship of a wide range of conferences related to hazardous substance management within EPA Regions 9 and 10.

Rationale: Conferences are a highly efficient and cost-effective way to achieve training and technology transfer.

Status: This year the Center cosponsored the following conferences:

International Symposium on In-Situ and On-Site Bioreclamation, March 19-21, 1991,
San Diego, California.

1991 Regional Conference on Hazardous Materials and Wastes, April 23-24, 1991,
Pocatello, Idaho.

Environmental Programs: Challenges for the 1990s, National Conference of the National University Continuing Education Association, May 13-14, San Diego, California.

New Development in Hazardous Waste Management, May 16, 1991, Oregon State University, Corvallis, Oregon.

Five-Centers' On-Site Bioremediation Conference, May 19-22, 1991, Gull Lake, Michigan.

Sixth Conference on Environmental Engineering Education, August 18-20, Oregon State University, Corvallis, Oregon.

Hazardous Materials Management Conference and Trade Show, September 16 and 17, 1991, Portland, Oregon.

Five-Centers' Conference on Technology Transfer, November 12-14, Fallen Leaf Lake, California.

WRHSRC PUBLICATIONS

Documents either published or submitted for publication during this year of Center activity are as follows:

A. Refereed Journal Articles

Alvarez, L. M., and P. L. McCarty, "Effects of Toxicity, Aeration, and Reductant Supply on Trichloroethylene Transformation by a Mixed Methanotrophic Culture," *Applied and Environmental Microbiology*, **57**(1), 228-235 (1991a).

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McCarty, P. L., "Engineering Concepts for In-Situ Bioremediation," *Journal of Hazardous Materials*, **28**, 1-11 (1991).

B. Articles Submitted or in Press

Alvarez-Cohen, L., P. L. McCarty, E. Boulygina, R. S. Hanson, G. A. Brusseau, and H. C. Tsien, "Characterization of a Methane-Utilizing Bacterium from a Bacterial Consortium that Rapidly Degrades Trichloroethylene and Chloroform," (submitted 1991).

Alvarez-Cohen, L., P. L. McCarty, and P. V. Roberts, "The Effects of Sorption on the Biotransformation Rate of TCE by Methanotrophs--Experiments with a Synthetic Zeolite," (submitted 1991).

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Chrysikopoulos, C. V., P. K. Kitanidis, and P. V. Roberts, "Macrodispersion of Sorbing Solutes in Heterogeneous Porous Formations in Spatially-Periodic Retardation and Velocity Field," accepted for publication in *Water Resources Research*, 1991.

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Edwards, E. A., L. E. Wills, M. Reinhard, and Dunja Grbić -Galić , "Anaerobic Degradation of Toluene and Xylenes by Aquifer Microorganisms Under Sulphate-Reducing Conditions," (submitted 1991a).

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Nicholson, D. K., S. L. Woods, J. D. Istok, and D. C. Peek, "Reductive Dechlorination of Chlorophenols by a Pentachlorophenol-Acclimated Methanogenic Consortium," (submitted 1991).

C. Chapters in Other Books or Bound Proceedings

Ball, H. A., M. Reinhard, and P. L. McCarty, "Biotransformation of Monoaromatic Hydrocarbons Under Anoxic Conditions," in *In-Situ Bioreclamation: Applications and*

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- Dawson, K. J. and J. D. Istok, *Aquifer Testing: A Manual for the Design and Analysis of Pumping Tests*, Lewis Publishers, Inc, Chelsea, Michigan (accepted, 1990).
- Edwards, E. A., L. E. Wills, D. Grbić -Galić , and M. Reinhard, "Anaerobic Degradation of Toluene and Xylene--Evidence for Sulphate as the Terminal Electron Acceptor," in *In Situ Bioreclamation: Applications and Investigations for Hydrocarbon and Contaminated Site Remediation*, R. E. Hinchee and R. F. Olfenbuttel, Eds., Butterworth-Heinemann, Boston, pp. 463-471 (1991b).
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- Grbić -Galić , D., S. M. Henry, E. M. Godsy, E. Edwards, and K. P. Mayer, "Anaerobic Degradation of Aromatic Hydrocarbons and Aerobic Degradation of Trichloroethylene by Subsurface Microorganisms," in *Organic Substances and Sediments in Water, Vol. 3: Biological.*, R. A. Baker, Ed., Lewis Publ., Inc., Chelsea, pp. 239-266 (1991).
- Little, C. D., C. D. Fraley, M. P. McCann, and A. Matin, "Use of Bacterial Stress Promoters to Induce Biodegradation Under Conditions of Environmental Stress," in *On-Site Bioreclamation, Processes for Xenobiotic and Hydrocarbon Treatment*, R. E. Hinchee and R. F. Olfenbuttel, Eds., Butterworth-Heinemann, Boston, pp. 493-498 (1991).
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D. Project Reports

- Amierreh Saberiyan, "Kinetic Model of Pentachlorophenol Degradation by Microorganisms," Engineering Project, Oregon State University, 1991.
- Grathwohl, P., and M. Reinhard, "Sorption and Desorption Kinetics of Trichloroethene in Aquifer Material under Saturated Conditions," Technical Report No. WR-2, WRHSRC, Department of Civil Engineering, Stanford, CA (1991).

E. Theses/Dissertations

- Alvarez-Cohen, L., "Cometabolic Biotransformation of Trichloroethylene and Chloroform by Methanotrophs--Experimental Studies and Modeling of Toxicity and Sorption Effects," Ph.D. Dissertation, Stanford University, Stanford, CA (1991).
- Chrysikopoulos, C., "Solute Transport in Porous Media: Investigation of Well-to-Well Circulation and Analysis of Spatially Variable Retardation," Ph.D. Dissertation, Stanford University, Stanford, CA (1991).
- Cozza, C. L., "A Model for the Prediction of Biologically Mediated Reductive Dechlorination Pathways," M.S. Thesis, Oregon State University, Corvallis, OR (1990).
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- Peters, D., "Anaerobic and Aerobic Treatment of Chlorinated Phenols with Granular Activated Carbon Expanded Bed Reactors," M.S. Thesis, Oregon State University, Corvallis, OR, 1991.
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F. Conferences and Workshops Sponsored or Cosponsored

- "International Symposium on In-Situ and On-Site Bioreclamation," March 19-21, 1991, San Diego, California.
- "1991 Regional Conference on Hazardous Materials and Wastes," April 23-24, 1991, Pocatello, Idaho.
- "Environmental Programs: Challenges for the 1990s, National Conference of the National University Continuing Education Association," May 13-14, San Diego, California.
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- "Sixth Conference on Environmental Engineering Education," August 18-20, 1991, Oregon State University, Corvallis, Oregon.
- "Hazardous Materials Management Conference and Trade Show," September 16 and 17, 1991, Portland, Oregon.
- "Biological Transformations of Chlorinated Solvents in Subsurface Systems—Natural Processes and in-Situ Bioremediation," One-day workshop held October 4, 1991, in Pasadena, California.

"Five-Centers' Conference on Technology Transfer," November 12-14, 1991, Fallen Leaf Lake, California.